DFT and experimental studies on synthesis of bisphenol a: Determination of optimal feed profile in semi-batch reactor

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KEYWORDS

DFT, BPA, Pulsed feed, Semi batch, Selectivity

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1 | Introduction

Bisphenol-A (BPA) is a very important material for production of polycarbonates, epoxy resins and many other polymers. BPA is synthesized with condensation reaction of phenol and acetone in acidic media (Figure 1).

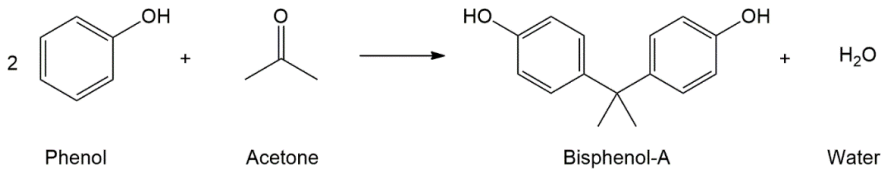

Figure 1 BPA synthesis reaction with phenol-acetone condensation.

Sulfuric acid and hydrochloric acid are used as catalyst for the traditional production method. Besides, ion-exchange resins extensively are used as catalyst in industry. BPA must have minimum 95% purity for the epoxy resin production and 99% and upper purity for the polycarbonate synthesis.[1,2] Depending on the reaction conditions and catalyst types, many by-products occurs in the process of BPA production. In the literature there are various studies to increase yield and selectivity. These studies generally are catalyst works conducted for the purpose of eliminating disadvantages of the mineral acid usage. The common property of these studies is feeding phenol to acetone molar ratio greater that to stochiometric ratio (from 3:1 to 10:1). The reason is to eliminate the by-products occurring self-condensation of acetone and the others.[2] However, operational cost, which includes pumping, heating, distillation, is increased with high phenol feeding in this way. As mentioned above high concentration of acetone in reaction media increases by-products due to self-condensation of acetone and side reactions. The most common by-products formed at the end of the reaction are summarized in Figure 2.

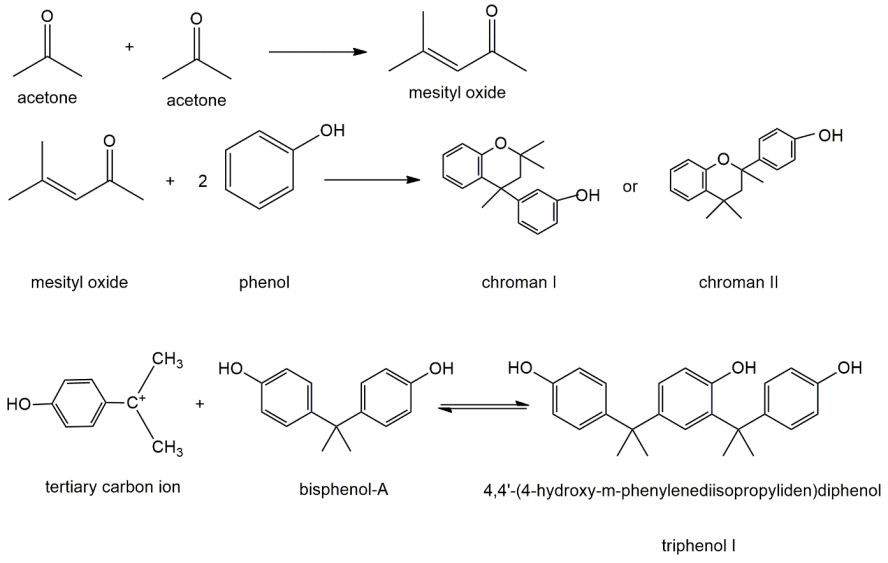

Figure 2 Formation of by-products with the high amount of acetone.

As known essentially in semi-batch systems, it is possible to manipulate the concentration of reactants in reaction media at the desired levels to obtain high yield and selectivity, also wild exothermic reactions can be controlled with these systems. There are different semi-batch studies based on yield and selectivity in literature. Because of its industrial importance, works conducted on BPA synthesis are generally encountered in the patent literature.[3-19] Nowinska and Kaleta synthesized a new catalyst with encapsulation of

12-tungstophosphoric acid (HPW), ammonium and cesium salts on the MCM-41 for liquid phase BPA production. They compared yield and selectivity with synthesized catalyzer and zeolite (H-Y, H-DY). They carried out experiments at certain temperatures, reaction times and phenol-acetone molar ratios. They found highest selectivity (%60) with CsHPW/MCM catalyzer, feeding of 3:1 phenol-acetone molar ratio, at 160° in 6 hours.[3] Jerabek and his colleagues used ion-exchange resins as catalyzer to synthesize BPA. They chose sulfonated divinyl benzene and Amberlyst as catalyzer. They investigated activity and the swelling properties of these catalyzers. They used CSTR microreactor to prevent the problems that come with catalyzer swelling in batch systems. They achieved the highest reaction rate with sulfonated divinyl benzene (%1 by weight), feeding ratio of phenol to acetone 8:1 at 70°.[4] Lastly, Maestri and Rota, compared semi-batch reactors and semi-batch recycle reactors which designed for preventing the further reaction of main products with by-products hence selectivity loss. They developed boundary diagrams which can be used to identify selectivity and reactor productivity just using operating conditions and with these diagrams no need to solve mathematical model of the system.[19] However, in all of these studies, bisphenol a synthesis could not be synthesized in an appropriate yield or amount. It is not considered appropriate for them to be produced on an industrial scale. In addition, many by-products were obtained.

Therefore, this study aims to eliminate the disadvantages (energy costs) of the pre-said situation. For this purpose, semi-batch reactor type was selected and experiments were conducted at stoichiometric ratio in various feeding modes. Acetone was fed as pulsed flow in a semi-batch operation. Feeding and waiting time were changed systematically and best result was explored for high yield and selectivity. Besides, batch and semi batch studies results, which were conducted in stoichiometric and over stoichiometric ratios were compared. The effect of mercaptoethanol as a catalyst enhancer, the amount of catalyst on product yield and selectivity was also investigated. As a result, the optimal feeding mode was determined to achieve high efficiency and selectivity with stoichiometric ratio aimed the minimum operating cost.

2 | Materials and methods

2.1 | Materials

Phenol, Amberlyst-15 and mercaptoethanol from Sigma Aldrich, acetone and 37% HCl from Carla Erba were used in these all experiments. Shimadzu GC-FID/2014 was used for the analysis. The method of analysis was found in literature.[20] The analysis method is as follows: The first 2 minutes column temperature is 50 @C. The column temperature increases to 250 °C with a ramp that lasts for 4 minutes with an increase of 50 °C per minute. Then the column temperature is held at 250 °C for 6 minutes. The detector temperature is 320 @C. Thus, the total analysis time for a sample is 12 minutes.

2.2 | Experimental Setup and Procedure

BPA production reaction which results from the reaction of 2 moles of phenol with 1 mol of acetone. In practice, this reaction cannot be carried out efficiently using stoichiometric ratios. This is due to the formation of isomers and derivatives of BPA and the self-condensation of acetone in series and parallel reactions.[21] In order to prevent this, practically high phenol:acetone ratios are preferred. This ensures that the acetone concentration is kept low in the reaction medium. But this will actually lead to an increase in energy costs as well. Based on this challenge, the operating conditions of the semi-batch reactor using stoichiometric phenol/acetone ratio were investigated.

In semi-batch experiments, 0.4 moles of acetone were fed into the reactor during the 6 hours reaction time that previously added 0.8 moles of phenol, at various flow modes (pulsed mode). In order to keep the concentration of acetone in the media to a low level, it was fed to the reaction medium in a semi-batch condition. The semi-batch feeding was performed in various modes (45-15, 50-10, 60-30, 75-15, 90-30, 120-60, 180-180, 360-0 and batch 1-359). Some of these modes are shown in Figure S1.

In these modes the first term indicates the feeding time as minute and the seconds referee the waiting time (stopping the feeding). In the experiments firstly, 37% HCl was used as catalyst and 5%, 15% and 25% of the total reactants by mole were added to the medium. The reactants were stirred at 800 rpm and reacted

at 60 ° C and the reaction continued for 6 hours. Samples were taken at 4, 5 and 6th hours and analyzed. In addition, solid Amberlyst ion-exchange resin was also used as catalyst. Catalyst was added 10%(w/w) of the reactants to the reaction medium. In batch experiments, phenol and acetone were added to the reactor at a various molar ratios and the experiments were carried out under the above conditions. The results were compared with the experiments performed at 2:1, 3.5:1 and 5:1 etc. molar ratios of phenol-acetone. The semi-batch experiment system is shown in Figure 3.

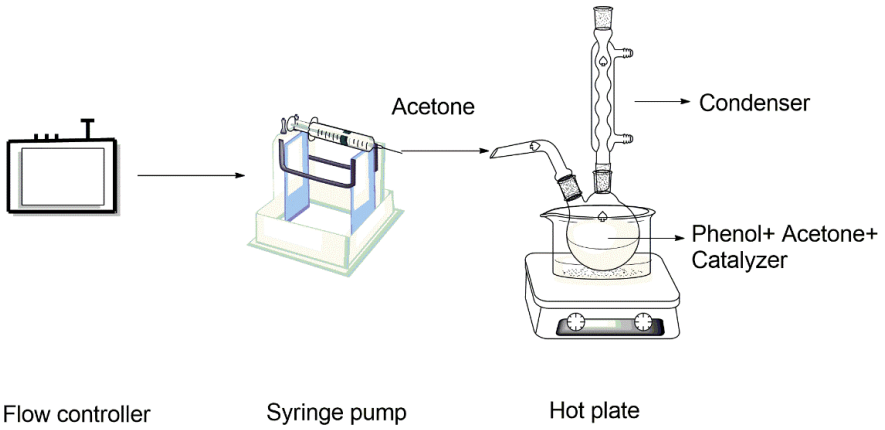

Figure 3 Semi-batch system for BPA synthesis by phenol-acetone condensation.

2.3 | DFT Calculations

The bisphenol a was obtained from the reaction of phenol with acetone, but, many by-products can be formed in addition to the target product. In this section, the reaction mechanism is theoretically examined and the energies of the bisphenol a and by-product, TS and intermediate are calculated. Thus, the formation possibilities of products and by-products were investigated theoretically. All molecules were optimized using Density functional theory (DFT)/B3LYP method[22] and 6-311++G(d,p) basis set. In addition, harmonic frequencies of the structures were calculated at the same method and basis sets to find a local minima (all positive force constants) or transition states (one imaginary force constant only). All calculations were performed with Gaussian 09 program package.[23]

2.4 | Modeling with Artificial Neural Network

Artificial neural networks (ANNs) method was used to modelling the obtained experimental data set so that to comprehend the results well. All computational and graphical operations were conducted in Matlab environment.

The algorithms that can simulate the functioning of the human brain, make decisions, draw conclusions, complete incomplete data, learn and remember are called "Artificial Neural Networks. As ANNs solve problems, which cannot be solved by classical methods, by means of similar to the working system of human brain, their performance is quite high. Artificial neural networks work by establishing structures similar to the neurons and the connections between them in the human brain. In general, ANNs working principle is nothing more than to optimize those connections. ANN, whose general structures consist of input, hidden and output layers, can be constructed from various architectures.[24-26] Here, the most common one, which feedforward structure, was used and Levenberg-Marquardt method was chosen as the optimization method. 70% of the available data set was used for training, 15% testing and 15% for the control. In the preliminary experiments, the number of neurons in the interlayer were taken as 10. Minimization of mean squared error was chosen as objective function for optimization process. Also, the 'tansig' function was used as a transfer function. General determined structure can be seen from Figure S2.

3 | Results and discussion

3.1 | DFT calculations

The most likely by-products that may occur in the bisphenol a synthesis have been determined from the literature. These byproducts are methicyl oxide, chroman I, chromanII and triphenol compounds. By examining each product and by-product mechanism, possible product, ancestor product and transition states that may occur are modeled. All defined molecules were optimized in DFT / 6-311 ++ G (d, p) method and base set. It has been proven that they are optimized at minimum energy by performing frequency calculations. Optimized structures and relative energies of the calculated molecules are shown in Figure 4, and the relative energy values are listed in Table 1.

When Figure 4 and Table 1 are examined, as a result of the reaction of phenol and acetone, the relative reaction energy of bisphenol a was calculated as -53.25 kJ / mol. It has been found that among possible intermediates, chroman molecules can be obtained with higher energy than bisphenol a. The relative energy of the chroman I and chroman II molecules was calculated as -65.13 and 65.32 kJ / mol, respectively. Other expected products indicate that the mesityl oxide compound may form as a by-product, although the formation of mesityl oxide and triphenol compounds is low. The step determining the reaction rate for all products and by-products is the first step. The relative energy of these steps was calculated as 184.98-233.12 kJ / mol. Although the reaction with the lowest transition state energy is bisphenol a, especially chroman compounds I and II are likely to form as byproducts. Small amounts of mesityl oxide and triphenol by-products are also expected to form. According to these results, synthesis and synthesis cost of a bisphenol molecule, which is widely used commercially, is very important. In this context, it is very important to get rid of by-products that are unavoidable during the reaction and to ensure that energy costs are minimized. For this reason, experimental studies are designed to reduce by-products and reduce raw material and energy costs in the following sections.

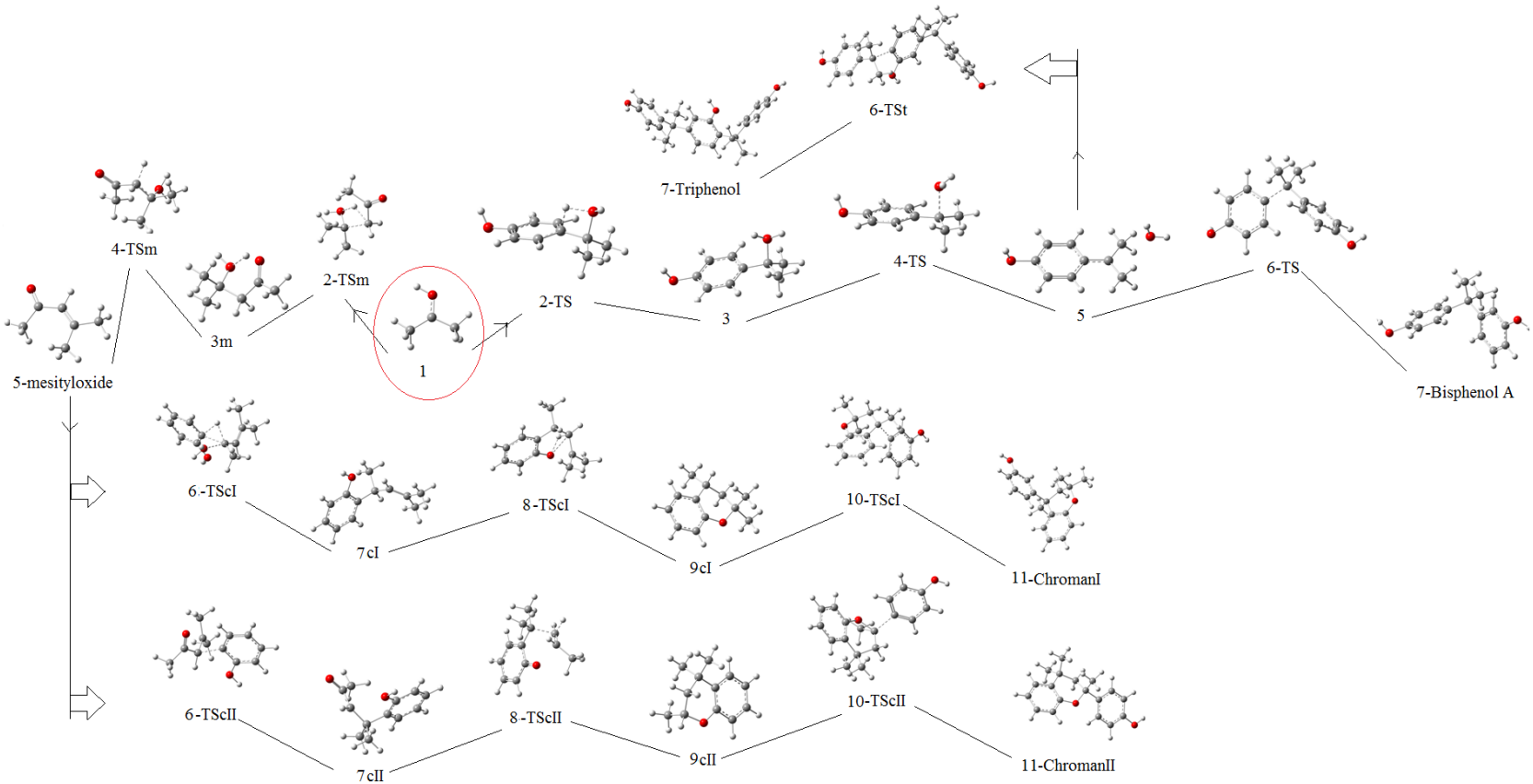

Figure 4 Relative energies between reactans, phenol + acetone and product as bisphenol a, by-product as mesityl oxide, chroman I, chroman II, triphenol I, and their TS, intermediate.

Table 1. Relative energy of the reaction paths for synthesis of bisphenol a and by-product, TS and intermediate.

Molecule	Relative energy (kJ/mol)
1	0.00
2-TS	184.98
3	36.33
4-TS	103.59
5	26.20
6-TS	156.85
7-Bisphenol A	-53.25
6-TSt	233.12
7-Tripyhenol	56.70
2-TSm	204.33
3m	105.72
4-TSm	193.02
5-mesityloxide	-8.55
6-TScI	193.42
7cI	54.48
8-TScI	110.43
9cI	29.35
10TSc1	128.65
11-ChromenI	-65.13
6-TScII	189.52
7cII	48.31
8-TScII	105.73
9cII	34.48
10-TScII	134.51
11-ChromenII	-65.32

3.2 | HCl catalyst results

The selectivity and conversion values obtained from semi-batch experiments in various feed modes using 5% HCl catalyst are given in Table 2. In general, conversion and selectivity are lower at 5% acid concentration. All selectivity values are below 91% from 0.81 and the average value is around 0.87±0.028. It is understood that the average conversion is around 26% ±0.035%. The selectivity tends to remain almost constant and conversions increasing are being observed over time.

An increase of approximately 15% in conversion between each hour, regardless of acid concentration is noticeable (Table 2). When the acid concentration increases from 5% to 15%, conversions increase by more than 60%. When the acid concentration increases from 15% to 25%, it is encountered that the increase in conversion is about 20%. Selectivity values between the modes do not show very obvious relationships because the acetone concentration in the medium varies with the feeding modes, and many series and parallel reactions in the reaction medium depend on this acetone concentration. When it is looked at the data, which 25% acid concentration is used, it is seen that the selectivity is 91% for continues feeding mode (360-0) and 88% for batch mode (1-359). Interestingly, the selectivity values for '60-30' feeding mode (similar to the other acid conc.) are lower than the other feeding modes, while the others showed almost similar selectivity.

Again, generally the highest conversion and selectivity are observed in cases where the acid concentrations

are 25%, as can be seen from Table 2. Although, 54% conversion and 95% selectivity are peak values, the selectivity shows an average value of 0.92 ±0.02. In the case of using 15% acid concentration, the values of selectivity (94%) belong to the 5th and 6th hours of '45-15' feeding mode are close to the values when using 25% acid concentration. Selectivity value is 89% at 15% acid concentration in 180-180 feeding mode. Also '90-30' feeding mode shows similar performance. The '45 -15' mode is therefore used as the basis for conducting further trials. As can be seen from the tables, in many trials, the impurities actually occur during the first 4th hour, after which they either fall or remain almost constant.

The higher selectivity values at the 15% acid concentration in the '45-15' feeding mode (the need for low acid usage) led to the progression through this mode as previously mentioned. Afterwards, studies were conducted in over ratios (3.5/1, 5/1) in '45-15' feeding mode. The effect of co-catalyst usage was also investigated in batch and semi-batch systems. The results are given in Table 2.

Table 2. The results of experiments performed with HCl catalyst.

Feeding Mode (min-min)	Phenol/ Acetone	HCl %	4th hour	4th hour	5th hour	5th hour	6th hour	6th hou
			Selectivity	Yield	Selectivity	Yield	Selectivity	Yield.
using 5% HCl as catalyst	using 5% HCl as catalyst	using 5% HCl as catalyst	using 5% HCl as catalyst	using 5% HCl as catalyst	using 5% HCl as catalyst	using 5% HCl as catalyst	using 5% HCl as catalyst	using 5% HCl as catalyst
45-15	2:1	5	0.85	0.16	0.86	0.21	0.86	0.30
50-10	2:1	5	0.89	0.24	0.88	0.25	0.88	0.29
60-30	2:1	5	0.86	0.21	0.87	0.24	0.85	0.25
75-15	2:1	5	0.81	0.17	0.89	0.23	0.90	0.27
90-30	2:1	5	0.89	0.16	0.90	0.20	0.90	0.40
360-0	2:1	5	0.88	0.15	0.89	0.17	0.88	0.19
180-180	2:1	5	0.89	0.22	0.89	0.25	0.88	0.27
120-60	2:1	5	0.87	0.23	0.87	0.25	0.91	0.37
1-359	2:1	5	0.81	0.10	0.81	0.12	0.82	0.13
using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst
1-359	2:1	15	0.88	0.28	0.89	0.32	0.90	0.35
45-15	2:1	15	0.92	0.26	0.94	0.34	0.94	0.46
50-10	2:1	15	0.82	0.28	0.91	0.38	0.90	0.45
60-30	2:1	15	0.89	0.29	0.89	0.35	0.90	0.38
75-15	2:1	15	0.93	0.32	0.93	0.38	0.93	0.40
90-30	2:1	15	0.90	0.32	0.91	0.39	0.93	0.44
120-60	2:1	15	0.93	0.34	0.91	0.37	0.91	0.41
180-180	2:1	15	0.88	0.33	0.89	0.36	0.89	0.39
360-0	2:1	15	0.91	0.23	0.91	0.25	0.93	0.33
using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst
1-359	2:1	25	0.92	0.40	0.90	0.44	0.91	0.46
45-15	2:1	25	0.92	0.35	0.94	0.42	0.94	0.47
50-10	2:1	25	0.91	0.39	0.93	0.47	0.93	0.48

Feeding Mode (min-min)	Phenol/ Acetone	HCl %	4th hour	4th hour	5th hour	5th hour	6th hour	6th hou
60-30	2:1	25	0.89	0.36	0.89	0.41	0.90	0.46
75-15	2:1	25	0.93	0.36	0.94	0.42	0.94	0.46
90-30	2:1	25	0.94	0.39	0.94	0.45	0.94	0.50
120-60	2:1	25	0.93	0.42	0.92	0.46	0.93	0.51
180-180	2:1	25	0.95	0.49	0.94	0.51	0.95	0.54
360-0	2:1	25	0.89	0.34	0.89	0.41	0.88	0.49
use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst
45-15	5:1	25	0.92	0.53	0.92	0.65	0.88	0.72
45-15	3.5:1	25	0.95	0.49	0.94	0.62	0.95	0.69
45-15+co	2:1	25	0.97	0.57	0.95	0.59	0.97	0.60
1-359+co	2:1	25	0.82	0.5	0.85	0.56	0.85	0.60

In the case where 25% HCl and the co-catalyst are used, 97% selectivity was attained at 6th hours. Although, the conversions in the 3.5/1 and 5/1 mole ratios are higher than stochiometric ratio '45-15' feeding mode, the selectivity's are lower. In these experiments, no co-catalyst was used, and if used, it is estimated that it would provide a 20 percent increase in returns and improvements in selectivity would be observed. Again, in the case of batch stochiometric run was carried out with co-catalyst, the conversion increased from 49% to 60% and the selectivity increased from 85% to 91%.

By-products form undesired colors as mentioned before. In Figure S3 it can be seen that differences of the samples obtained from batch and semi-batch systems in the color base. Lighter color obtained with semi-batch system. Parameters are same for both experiments except semi-batch was applied with 45-15 feeding mode.

3.3 | Amberlyst catalyst results

After the studies with HCl catalyst, studies were conducted with Amberlyst which is more environmentally friendly and simple to separate from the reaction medium. The results are given in Table 3. In the studies conducted with Amberlyst catalyst, 2.3% conversion was achieved in the batchexperiment, while this value remained at 1.4% in the '45-15' feeding mode, also 50% increase in selectivity is observed. In the batch run with the co-catalyst, the conversion was increased to 3% and the selectivity increased to 94%. It is understood that the co-catalyst has a great effect on selectivity here. In the trial where the excess ratio was studied (5-1), the conversion reached 5% and the selectivity remained at 66%. Again, it is obvious in the case of using co-catalyst a positive contribution in conversion and selectivity is possible. As a result, it is understood that in the '45-15' mode, with 15% HCl catalyst, high conversion and selectivity can be achieved without spending too much HCl. The Amberlyst catalyst, although environmentalist, is inadequate in conversion. The use of co-catalyst provides significant improvement in the system in all cases.

Table 3. The results of experiments performed with Amberlyst catalyst.

Phenol/ Acetone	4th hour	4th hour	5th hour	5th hour	6th hour	6th hour
	Selectivity	Yield	Selectivity	Yield	Selectivity	Yield
2-1 (batch)	0.50	0.012	0.50	0.018	0.43	0.023

Phenol/ Acetone	4th hour	4th hour	5th hour	5th hour	6th hour	6th hour
2:1 (45-15)	0.75	0.01	0.53	0.013	0.64	0.014
5-1 (batch)	0.57	0.04	0.61	0.048	0.66	0.052
2:1 (batch)+co	0.88	0.024	0.9	0.028	0.94	0.03

3.4 | Chemcad simulation

The Chemcad program was used to calculate the heat loads required for the distillation column and the energy required for pre-heating and reactor cooling. This simulation was conducted based on the conversion data obtained from the experiments. The results are given in Table 4.

Table 4. Energy requirements obtained by Chemcad simulation program.

Mole ratio	Feeding Mode	x (%)	Distillation Condenser (kJ)	Distillation Reboiler (kJ)	Reactor (kJ)	Heat Exchanger (pre heater) (kJ)
10-1	1-359	100	-82384.1	95476	-15850	12736
5-1	45-15	72	-37742.9	47627.1	-11440.1	6863
3.5-1	45-15	69	-22145.6	30548.2	-10968.9	5091.8
2-1	45-15+co-cat.	60	-9346.56	16671.5	-9576.2	3334

The data in the Table 4 were handled on the basis of 10 kg acetone. Acetone was pre-heated with stoichiometric or excess phenol and then fed into the reactor. The energy calculation was examined based on the conversion in the experimental results. Then the mixture obtained from the reactor was subjected to distillation and the heat loads required for the boiler and condenser were examined. Preliminary trials have shown that the change in the number of trays does not substantially change the amount of energy required for the condenser and the reboiler. This brings up the results of the following; the difference between the boiling points of phenol and

BPA is too high, therefore effect of the number of trays to be low. It was observed that the amount of energy consumed in the condenser and reboiler increased with the increase in reflux rates while the number of trays was constant. However, the separation time was reduced but this did not decrease significantly. The amount and duration of energy required for the separation to be realized was determined by simulation. All experiments were carried out for a column with 5 trays and reflux rate of 0.25. A total of 95476 kJ of energy is required as a result of the batch experiment with a phenol-acetone feed at a molar ratio of 10:1, and 16671 kJ of energy is required in a 2:1 molar ratio. Increase in the amount of phenol appears to increase the amount of energy in the boiler about 6 times. Again, the energy requirement in the condenser is about 9 times higher It is seen that 4 times more energy is needed for pre-heating and about 1.5 times more energy is required for reactor cooling.

3.5 | ANN results

The data set consisting of 96 data were used for artificial neural network modeling. Of this set, 68 were allocated for training, 14 for testing and 14 for control data. In order for the network not to memorize, learning should take place properly, the data set should be blended well, and the training test and control

data should be selected homogeneously. For this purpose, a series of experiments were performed with different initial condition, and the situation where all of the R^2 were high was investigated. There are 6 input variables and 1 output variable in the general structure of the network. The value of hidden layer size was tried to be determined by preliminary experiments. Conversion was selected as output variable. Network structure with 2 outputs (conversion and selectivity) and single output (only selectivity) were also studied, but positive results could not be obtained from here. It has already been mentioned in the previous chapters that a significant correlation between the selectivity value and the feeding modes could not be seen. Here 6 input variables are; phenol/acetone ratio, co-catalyst usage state (0/1), feed time, waiting time, acid concentration and reaction time. The regression graphs obtained by plotting the conversion values in experimental data against the results of the network are given in Figure S4.

As can be seen, the network performed well for both training, test and control data, 0.99 R^2 values were obtained for all. High training R^2 is important because low means the network is not well trained. This value indicates the educational performance of the network, but only if this value is high this does not make sense. Higher R^2 of test and control data are also desirable, otherwise, the network have memorized and cannot predict when new situations occur. After this point, 3-D graphics were drawn in MATLAB using the obtained neural network model. Conversion against time /HCl (%), conversion against time /mol ratio graphs are shown in Figure 5.

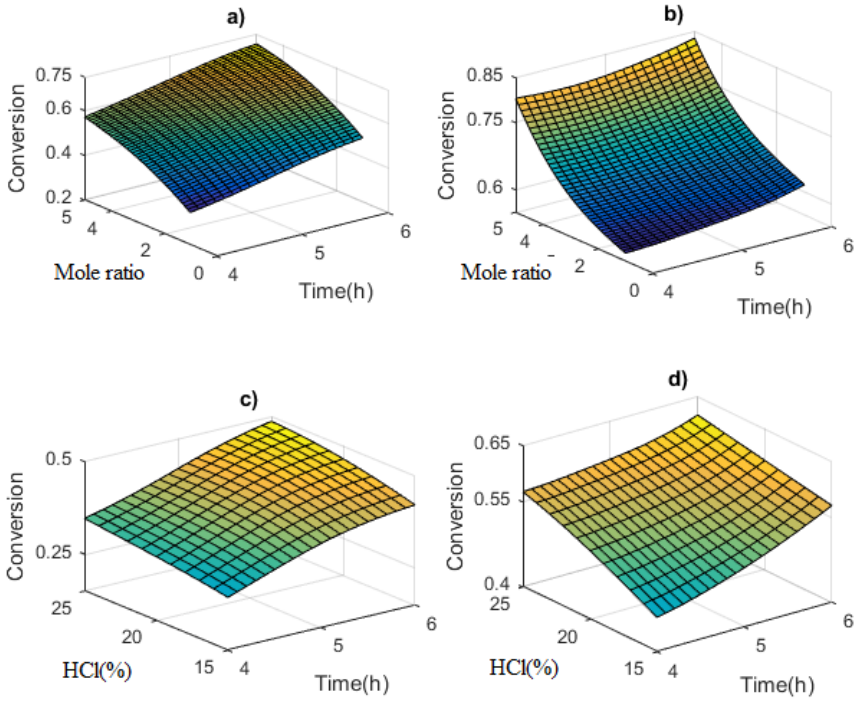

Figure 5 '45-15' feeding mode a) conversion against time /mol ratio without co-catalyst b) conversion against time /mol ratio without co-catalyst c) conversion against time/HCl (%) without co-catalyst, d) conversion against time/HCl (%) with co-catalyst.

The first thing that stands out in the graphs is that when the co-catalyst is used, the structure of the graphs shifts from concave to convex. Figure 5-b shows that if trial was performed for '45-15' feeding mode with co-catalyst at a 5/1 molar ratio, 83% conversion would be achieved in 6th hours. In '45-15' feeding mode, when 2/1 mole ratio is used with 25% HCl, the conversion increases from 50% to 60% by using co-catalyst.

It is also seen from the graphs that the molar ratio makes a steeper output in the form of the graph and the change over time is smoother.

4 | Conclusions

In the bisphenol a synthesis reaction, different by-products are obtained with many serial and parallel reactions. This result has also been demonstrated as a result of DFT studies, in this paper. Therefore, the solution proposal was investigated in the laboratory environment. Originated high concentration of acetone, high molar phenol/acetone ratios are being used in the industry to prevent serial and parallel reactions in the reaction medium. This imposes energy costs on the plant. Studies in this paper were carried out based on above challenge. In a semi-batch reactor working at stoichiometric ratios, acetone feed profile which will achieve high conversion and selectivity also the effect of catalyst type and concentration of HCl were investigated. It has been found that '45-15' feeding modes are the best among the various feed profiles. Also, the amount of HCl increased from 5% to 15% conversions increased by 60% and increasing HCl percent from 15% to 25% conversion increased around 20%. With the increase of the amount of HCl from 5% to 15%, the selectivity has increased from 87% to 91.5%. The highest conversion with the Amberlyst catalyst was obtained as 5.1 with 5/1 phenol-acetone ratio with a selectivity of 60%. Using Amberlyst in the presence of co-catalyst in the stoichiometric ratio, the selectivity increased from 64% to 94% and conversion from 1.4% to 3%. The use of co-catalyst has been shown to contribute positively to conversion and selectivity in all cases. The energy required for reboiler in the distillation column is 95476 in the case of 100% acetone conversion at molar ratio of 10/1 mol. In the case of 60% conversion at molar ratio of 2/1 and co-catalyst usage, the energy requirement is 16671. It is understood that the energy requirement is 6 times greater. While 60% conversion and %85 selectivity were obtained at molar ratio of 2/1. In the '45-15' feeding mode 60% conversion and 97% selectivity were achieved. At this manner effective result was obtained both energy and selectivity aspects. After these, an ANN model was obtained with the obtained experimental data. Feeding time, waiting time, HCl percent and reaction time were selected as input parameters of the model. Only conversion, only selectivity and both of them were examined respectively as output. Although high correlations could not be obtained in the cases where selectivity was involved, high regression coefficients were obtained for conversion and the model predictions were plotted. As a result, pulsed feed semi-batch reactors are seen as usable in many similar processes in the energy, selectivity and efficiency axis.

Supplementary Information (SI)

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/.....

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Compliance with ethical standards

Conflicts of interest

There are no conflicts to declare.

Author contribution

Bugra AKMAN: Software, Validation, Formal analysis, Investigation, Data Curation, Writing- Original Draft, Ömür ARAS: Conceptualization, Methodology, Software, Formal Analysis, Data Curation, Writing-Original Draft, Visualization, Supervision, Project Administration, Funding acquisition, Yunus KAYA: Formal Analysis, Resources, Data Curation, Funding acquisition

Code availability

MATLAB 2020A and CHEMCAD 7.1.4 which provided by Computer labs. of Bursa Technical University used in this study. Figures were created by Microsoft Paint, MATLAB 2020A and ChemBioDraw Ultra 12.0

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